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CADMIUM POISONING
OF OXYGEN REDUCTION
ON PLATINUM ELECTRODE
IN POTASSIUM HYDROXIDE

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Cleveland, Ohio 44135

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16. Abstract <p>Experiment with a rotating disk and ring apparatus showed no poisoning by cadmium in 8.5 M KOH, alone or with Cl^- or $\text{CO}_3^{=}$. Poisoning does not occur either in 0.1 M KOH supernatant to CdO, but a partially reversible poisoning results from 10^{-4} M CdCl_2. A much more catastrophic poisoning occurs in 0.1 M KOH when both 10^{-4} M CdCl_2 and traces of fatty acid are present. Evidence indicates that the catastrophic poisoning affects the four-electron O_2 reduction more than it does the one-electron H_3O^+ discharge.</p>					
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CADMIUM POISONING OF OXYGEN REDUCTION ON PLATINUM

ELECTRODE IN POTASSIUM HYDROXIDE

by Riley O. Miller

Lewis Research Center

SUMMARY

Experiments with rotating ring and disk electrodes show that bright platinum (Pt) is not significantly poisoned by 8.5 M potassium hydroxide (KOH), supernatant to brown cadmium oxide (CdO) alone or containing dissolved cadmium chloride (CdCl_2) (10^{-4} M) alone, or with 0.1 M Cl^- with or without 0.5 M $\text{CO}_3^{=}$. Solid CdO does not produce poisoning in 0.1 M KOH either, but 10^{-4} M CdCl_2 does cause a partially reversible decrease in electrocatalytic activity. A new kind of nonreversible catastrophic poisoning in 0.1 M KOH was discovered when traces of both Cd^{++} and fatty acid are present. At a rotational speed of 60 revolutions per second during cathodic and anodic sweeps between 0.1 and ~ 1 volt against a standard hydrogen electrode in the same solution (SHE-SS), the electrocatalytic activity of bright platinum decreases roughly exponentially with half times of 20 to 30 minutes. At a constant potential of 0.100 volt against SHE-SS, extrapolation of measurements, made at 20 to 60 revolutions per second, show (after a period of 25 min) an electrocatalytic half time of only 10 minutes (later increasing four-fold). The results indicate the presence of the one-electron H_3O^+ discharge (expected at 0.1 V) and seem to show that this reaction is less poisoned by the catastrophic mode than is the four-electron oxygen (O_2) reduction.

INTRODUCTION

In principle the air-cadmium couple promises a secondary battery having long life and a practical energy density of perhaps 130 watt-hours per kilogram (60 W-hr/lb), based on a theoretical value of 445 watt-hours per kilogram (202 W-hr/lb). The critical part of such a cell is the gas electrode. Although platinum (Pt), so far, is the most efficient electrocatalyst for oxygen, it does lose electrocatalytic efficiency with use in air-cadmium cells (e. g., ref. 1). A possible reason for this loss may be that the

platinum is poisoned by slightly soluble cadmium (Cd) bearing ions. In the work described herein a rotating ring and disk (RRD) electrode was used to determine some of the conditions under which cadmium can poison bright Pt to oxygen reduction in KOH electrolytes.

SYMBOLS

E_d, E_r	potentials of disk and ring, respectively, V
I_d, I_r	total currents of disk and ring, respectively, mA
i_o	exchange current density, mA/cm ²
N	collection efficiency, hydrodynamically limited fraction of a species emanating at the disk that can be collected on the ring, dimensionless
r_1, r_2, r_3	radius of disk, inside and outside radii of ring
ω	rotational speed of electrode, rps, $2\pi/\text{sec}$

EXPERIMENTAL ASPECTS

Apparatus

The theory and practice of the rotating ring and disk (RRD) electrode have been reviewed (e.g., refs. 2 to 5). The RRD electrode and rotator was fabricated from the design of E. Yeager (ref. 4) by the machine shop at Case Western Reserve University. All parts in contact with the electrolyte were polyfluorocarbon or platinum. The reference potential was measured by a Luggin capillary normal to and about 1 millimeter from the center of the disk. The reference electrode was a commercial mercury - mercurous oxide (Hg-HgO) unit immersed in and bridged to the Luggin capillary by the same electrolyte that was used in the cell. (In the data presented, all potentials are converted to V against SHE-SS.) The cell had a 75-millimeter inside diameter and was 70 millimeters deep; the electrolyte depth was about 50 millimeters. The radii (r_1, r_2, r_3) of the disk and ring electrode were 2.50, 2.80, and 3.53 millimeters, respectively. The ring and disk were hand-polished to a mirror-like surface (finished with 0.05 μm alumina in water on a napped cloth). The polished electrode assembly, in turn, was soaked in concentrated nitric acid (HNO_3) and distilled water; then the ring was lightly platinized for 1 minute at 30 milliamperes in a solution of 2 percent $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in 2 M HCl (plus a small amount of $\text{PbC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$). (A dark bronze

colored surface on the ring resulted.) The RRD electrode assembly was soaked again in concentrated HNO_3 and washed and stored in distilled water.

The cell also contained two stationary electrodes consisting of wattles of 1-millimeter-diameter, 200-millimeter-long platinum wire held vertically and opposite to each other at the perimeter of the cell. Both of these were platinized to a smooth black surface. One served as a "gettering" electrode for solution purification, the other as the counter electrode. These were also soaked in HNO_3 and in distilled water, respectively, after platinization.

After platinization and washing, all electrodes (including RRD) were electrolyzed at 0.5 volt against SHE-SS for several hours, respectively, in two separate batches of dilute KOH solution, a procedure recommended by J. Giner (ref. 6).

The cell was always operated at room temperature and 1 atmosphere pressure. Before and during measurements of O_2 reduction, purified oxygen was fed to the cell through a polyfluorocarbon bubble tube near the cell's bottom. During gettering and electrode pretreatment operations, the KOH electrolytes were saturated with the purified argon gas in the same way.

Materials

The 0.1 M KOH electrolytes were made from boiled distilled water and reagent-grade KOH. Usually the water (~200 ml) was syphoned into the cell (which was flushed with argon) through a closed borosilicate glass system, and the preweighed KOH was added quickly from a stoppered weighing bottle.

When 8.5 M KOH was required, it was prepared in the cell by dilution of 45.5 percent by weight mercury-cell-grade KOH liquor with boiled distilled water. The 45.5 percent KOH liquor was delivered by the manufacturer in a polypropylene-lined steel drum from which approximately 4 liters was removed and stored in a closed all-polyfluorocarbon bottle-and-syphon system. This was wrapped with several layers of aluminum foil to minimize diffusion of carbon dioxide (CO_2), and other airborne impurities.

When additives to an electrolyte were required, they were admitted to the cell as 1-milliliter aliquots (if they were soluble) or as preweighed solids. All inorganic additives were reagent grade or higher purity.

The oxygen gas was from a cylinder that had been pressurized by boiling liquid oxygen. Before entering the cell, the O_2 gas passed through a bed of CuO at $\sim 700^\circ \text{C}$ and adsorbants for CO_2 and H_2O . The argon gas was 4N8 purity, water pumped.

Instrumentation

The one special instrument used in these experiments was a dual potentiostat which controlled independently the disk and the ring potentials E_d and E_r against the reference electrode. This instrument, a close adaptation of one described in the literature (ref. 7)¹ used commercial operational amplifier modules and provided indirect readouts of I_d , I_r , E_d , and E_r , respectively. The current readouts I_d and I_r , were plotted as y , respectively, against the readout of applied disk potential E_d as x on two separate commercial potentiometer recorders.

The ring potential E_r was kept nearly constant at $+1.40 \pm 0.02$ volts against SHE-SS. Preliminary experiments showed that the difference in I_r at E_d (equilibrium) and at E_d of 0.4 volt against SHE-SS varied little with E_r in the neighborhood of +1.4 volts E_r (against SHE-SS), and thus all the intermediate reaching the ring is oxidized. Similar results were reported by Genshaw (ref. 5).

As required, the input potential used to control E_d was ramped by a commercially available motor-driven helical potentiometer. The various potentials to the x-y plotters were monitored with a digital voltmeter having a maximum sensitivity of 0.02 millivolt.

Verification of Procedure

Figure 1 is offered in evidence that the experimental procedure used herewith gives valid electrochemical measurements. The lower dashed curve shows a dip in disk current I_d at approximately 0 volt against SHE-SS in nongettered 0.1 M KOH. However, when $I_r/0.36$ was added to I_d , giving the current equivalent to the four electron reduction of O_2 , the curve is flat in the transport-limited region (0 to ~ 0.6 V against H_2). The value 0.36 is the theoretical collection efficiency N read from reference 8. Similar results have been reported elsewhere (ref. 9).

The solid curves (fig. 1) show that less intermediate formed after the 0.1 M KOH was gettered. In various runs made with 0.1 M KOH, values of I_d/I_r were seldom as low as those obtained by Genshaw (ref. 5). Some determinations with an aged RRD electrode in ungettered 0.1-millimeter KOH were fairly comparable, but a clean electrode in gettered 0.1 M KOH gave I_d/I_r values three to 30 times greater than Genshaw. The importance of electrode and electrolyte conditions is emphasized also by the results of Giner (ref. 6), which show I_d/I_r values two to 20 times higher than comparable Genshaw data.

¹It should be noted that when R_4' (ref. 7) is properly adjusted, the F-2 output will read twice E'_{sig} instead of equal to E'_{sig} as stated in the last paragraph on p. 481 of the reference.

RESULTS AND DISCUSSION

Cadmium Alone

Cadmium was introduced in two alternative ways, either as solid brown cadmium oxide (CdO) or as cadmium chloride (CdCl_2) dissolved in a small aliquot of water. Experiments were made in concentrations of 8.5 and 0.1 M KOH, respectively.

In gettered 8.5 M KOH, disk currents I_d at potentials sweeps between 0 and +1.2 volts against SHE-SS show polarization waves that are less clearly defined than those obtained in 0.1 M KOH. The rather poorly defined, transport-limited I_d plateaus are roughly 1/60th of these observed in 0.1 M KOH. A sixty-fold reduction would be expected from the lower solubility (ref. 10) and diffusivity (ref. 11) of oxygen in 8.5 M KOH (compared to 0.1 M).

The following treatments of the 8.5 M KOH electrolyte did not significantly change I_d at 60 revolutions per second:

(1) Solid CdO ($\sim 1.4 \times 10^{-4}$ M) added, and several sweeps made during a period of $1\frac{1}{4}$ hours.

(2) Sixty hours later. (The electrode had been pulled and soaked in distilled water during the interim.)

(3) Total CdO equivalent increased to 4.2×10^{-4} M by addition of more solid brown CdO .

(4) Chloride content brought to 0.1 M by addition of dry KCl.

(5) After 16 hours (electrode stored in distilled H_2O):

(6) Dissolved CdCl_2 added to give 10^{-4} M CdCl_2 .

(7) Carbonate increased to 0.5 M by addition of solid K_2CO_3 .

These results indicate that Cd_{II} alone (presumably as the $\text{Cd}(\text{OH})_3^-$ species) and in the presence of several inorganic anions does not significantly affect the electrochemical oxygen-reducing efficiency of Pt in 8.5 M KOH. The results of reference 6 corroborate these findings for 8.5 M KOH supernatant to CdO .

In 0.1 M KOH the affect of Cd_{II} is dependent on how it is introduced into the electrolyte. No poisoning is observed after CdO ($\sim 1.7 \times 10^{-4}$ M) is added, a result corroborated by reference 6. However, when a dissolved aliquot of CdCl_2 (to make 10^{-4} M) is added to a fresh, ungettered 0.1 M KOH electrolyte, a partially reversible mode of poisoning is observed. Examples of I_d against E_d waves are shown in figure 2. Figure 2 shows cathodic sweeps before and after CdCl_2 additions. The continuous curve shows a quasi-steady state reached during cycling between 1.1 and 0.1 volt against SHE-SS. (At these conditions the potential for the deposition of cadmium is approximately +0.02 V, <0.1 V.) The poisoning is increased after holding the disk at 0.1 volt for 5 minutes and is reversed and diminished by holding the disk 6 minutes at 1.4 volts

against SHE-SS. A reversible adsorption due to the presence of the Cd_{II} species from soluble $\text{Cd}(\text{ClO}_4)_2$ has been demonstrated in 1 M KOH (ref. 12).

Fatty Acids With and Without Cadmium

Addition of oleic acid (10^{-4} M) to fresh 0.1 M KOH produced the results shown in figure 3, which shows both I_d and I_r for anodic sweeps at 50 volts per hour. Some poisoning is indicated by the shift of the I_d wave to a more cathodic potential and the appearance of more intermediate product at 0.4 volt and less at 0 volt, a rather typical behavior mode for I_r which was observed also in other instances.

When CdCl_2 was added to the 0.1 M KOH already containing 10^{-4} M oleic acid, a catastrophic mode of poisoning resulted in that the polarization waves became increasingly more cathodic with time and the electrocatalytic effect of the bright platinum disk was essentially lost after 2 hours. This catastrophic poisoning was not reversed by electrochemical means. These results are shown in figure 4. The dashed curve shows in anodic sweeps the stabilized I_d wave from 0.1 M KOH + 10^{-4} M oleic acid, before the addition of CdCl_2 . The other numbered curves show successive waves after CdCl_2 ($\approx 10^{-4}$ M) was added.

This catastrophic poisoning is a synergistic effect requiring small concentrations of both CdCl_2 and fatty acid, and occurs regardless of which is added first. Figure 5 shows the results of adding the latter to the former. The dashed curve, similar to the continuous curve in figure 2; shows the quasi-steady-state anodic-direction I_d polarization wave after several sweeps reversing between 1.1 and 0.1 volt against SHE-SS in 10^{-4} M CdCl_2 . The other curves show the progressive poisoning after a small amount of floating-soap solution (COOR^-) was added.

The current I_d at a given E_d decreases with time in a roughly exponential way; as is shown by crossplots of figures 4 and 5 in figures 6 and 7, respectively. For the most part, the half times of electrocatalytic activity average 20 to 30 minutes in the two cases studied (at 60 rps). The decay rates generally are fairly independent of potential; possibly because sweeping the potential produced an average rate of site occlusion.

To determine more exactly how the catastrophic kind of poisoning develops at constant E_d , values of I_d and I_r against time were obtained at an E_d of +0.100 volt against SHE-SS (E_r , +1.40 V). The electrolyte, 0.1 M KOH + 10^{-4} M CdCl_2 + 10^{-4} M oleic acid, which had been used to get the data in figures 5 and 7, was allowed to stand 20 hours in the polyfluorocarbon cell. During this interim the RRD electrode had been removed, washed in turn in concentrated HNO_3 and dilute KOH, and stored in distilled water. After the 20-hour interval, the electrode was returned to the solution and continuous records of I_d and I_r were made. The speed of the electrode was alternated for roughly 1-minute periods at 20, 30, and 60 revolutions per second. Values of I_d

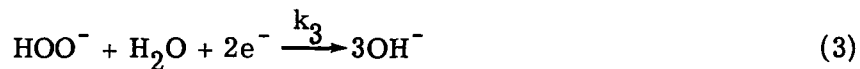
and I_r at 60 (circles) and 20 (squares) revolutions per second are shown in figure 8 plotted on logarithmic scales against time. Values of I_d , extrapolated to infinite rotational velocity are also shown (plotted as diamonds) for some selected time intervals. It is interesting to note that I_d increases and I_r falls for the first few minutes of operation. This seemed to indicate that the platinum has to "condition" itself for maximum catalytic efficiency. For over 25 minutes the disk current I_d is little affected by the poisoning process. The ring current I_r continues to decrease indicating a decrease in the concentration of intermediate (probably peroxide). An early warning of poisoning occurs at 20 minutes when I_r , and hence peroxide concentration, suddenly starts to increase. After 25 minutes the reaction-limited I_d (diamonds) suddenly decays at a half-time rate of 9.5 minutes. At about 50 minutes, the half time increases to about 36 minutes, almost a fourfold decrease in apparent rate of poisoning. During the interim of maximum I_d decrease, I_r peaks, declines, and then becomes constant after about 50 minutes (when I_d goes into its slower decay rate).

The evidence shows that, if anything, the electrocatalytic activity of the disk increases (at 0.1 V against SHE-SS) for as long as 20 minutes before the limiting effect of catastrophic poisoning is at all apparent. It is fairly common for an O_2 electrode to "condition" itself for optimum performance. The delay in the start of catastrophic poisoning thus far remains an intriguing problem and perhaps represents some sort of "initiation time" for the process.

The behavior of the ratio I_d/I_r with respect to rotational velocity ω can characterize to some extent the electrochemistry at the disk. Genshaw (ref. 5), for example, suggests that in alkaline solution two competing electrochemical reductions can occur at the disk. They will be indicated here as an overall four-electron reaction and a competing two-electron formation of an intermediate.



Part of the intermediate (in this example HOO^-) is reduced further at the disk,



and the rest goes into solution, the fraction N of which is oxidized as the disk (held at an anodic potential). For reactions of this sort the following relation was derived (ref. 5):

$$\frac{I_d}{I_r} = \frac{x+1}{N} + \frac{(x+2)k'}{N} \frac{1}{\omega^{1/2}} \quad [1]$$

where k' is a constant containing diffusivity, viscosity, and the rate of intermediate removal, reaction (3); and x is the ratio of the current in reaction (1) to the current in reaction (2).

The second term can only be greater than zero; that is, I_d/I_r will be constant or decrease with ω . The results of this work, however, show that, when E_d is kept at 0.100 volt against SHE-SS, the ratio I_d/I_r generally is greater at $\omega = 60$ revolutions per second than it is at 20 revolutions per second, opposite to what equation [1] requires. Another mechanism is involved and Genshaw (ref. 5, p. 361) has proposed an answer for this also. At I_d potentials near zero against SHE-SS, the reaction



becomes important and chemical reduction of O_2 can occur, for example,



Reaction (4) then competes with (1); but, at higher rotational speeds which increases O_2 transport, reaction (1) is favored, so that I_d/I_r increases with ω (as is observed in this work). For reaction (4), under the conditions of this experiment, I_d is computed to be 0.32 milliampere. The computation is based on a Tafel slope of 0.120 volt and i_o of 1.1×10^{-2} ampere per centimeter squared (suggested by ref. 5, p. 362).

It is interesting to conjecture how the catastrophic poisoning affects reactions (1) and (4). Two hypotheses will be examined briefly.

As a first guess one can speculate that, because of the mobility of H^+ and $H(Pt)$, catastrophic poisoning affects reaction (4) little, if at all. The current for reaction (4) would be constant (0.32 mA computed) for the total time interval (fig. 8). Indeed, the values of I_d in figure 8 after 80 minutes do seem to approach asymptotes surprisingly close to 0.32 milliampere.

One is tempted to speculate further. This time it is assumed that the one-electron reaction (e.g., (4)) is affected by poisoning. Suppose that after the onset of catastrophic poisoning, at about 25 minutes, reaction sites are being occluded at an exponentially decreasing rate. The nearly fourfold change (at 50 min) in slope of $\log I_d$ at $\omega = \infty$ (diamonds, fig. 8) could represent a transition from a four-electron reduction at each electrochemically active site to a one-electron discharge. At this stage of poisoning, one can imagine H_3O^+ discharge taking place at sites now forbidden to O_2 adsorption, and the reduction of O_2 taking place chemically (by migrating H atoms) at adsorption

sites that are not electrochemically active. If the second slope represents reaction (4) the clean-disk discharge current would be higher than 0.32 milliamperes. By backward extrapolation it would be 1.3 ± 0.2 milliamperes at 25 minutes, where overt poisoning becomes apparent. Noting that the chemically limited plateau for total I_d is about 5.8 milliamperes, dare one conjecture that catastrophic poisoning does not occur until after the rate of the one-electron reaction becomes equal to or less than the four-electron reaction? In this case, for example, the relative rate of the one-electron to the four-electron reaction is $1.3 \pm 0.2 / [(5.8 - 1.3 \pm 0.2) / 4] = 1.15 \pm 0.2$. Within experimental error, this ratio is unity at the onset of catastrophic poisoning.

Conjecture aside, the results do seem to show, not too surprisingly, that the four-electron O_2 reduction reaction is more vulnerable to the catastrophic kind of poisoning once it has started, than is the one-electron H_3O^+ discharge.

SUMMARY OF RESULTS

Experiments were made using a rotating ring and disk technique to assess the poisoning by cadmium of electrochemical oxygen reduction on bright platinum in potassium hydroxide (KOH) electrolyte.

1. No significant poisoning was found in either 0.1 or 8.5 KOH supernatant to solid brown CdO.

2. A quasi-reversible form of poisoning occurred in 0.1 M KOH containing 10^{-4} M cadmium chloride ($CdCl_2$). The extent of poisoning could be either increased or reversed to some extent by respective cathodic or anodic treatment. No significant poisoning occurred in 8.5 M KOH + 10^{-4} M $CdCl_2$.

3. A new kind of catastrophic poisoning was found in 0.1 M KOH containing small amounts of both $CdCl_2$ and fatty acid. This poisoning seemed to be electrochemically nonreversible. At 60 revolutions per second electrocatalytic activity decreased exponentially with half-lives of 20 to 30 minutes.

4. In 0.1 M KOH + 10^{-4} M oleic acid at a potential of 0.100 volt against SHE-SS, the extrapolated chemically limited current was roughly constant for 25 minutes and then decreased at 9.5 minutes half time rate for 25 minutes after which the half time became 36 minutes. A significant discharge of H_3O^+ and reaction of H absorbed on Pt is indicated at this potential. The one-electron H_3O^+ discharge reaction seems to be less affected by the catastrophic poisoning mode than is the four-electron reduction of O_2 .

Lewis Research Center,

National Aeronautics and Space Administration,

Cleveland, Ohio, May 8, 1972,

113-34.

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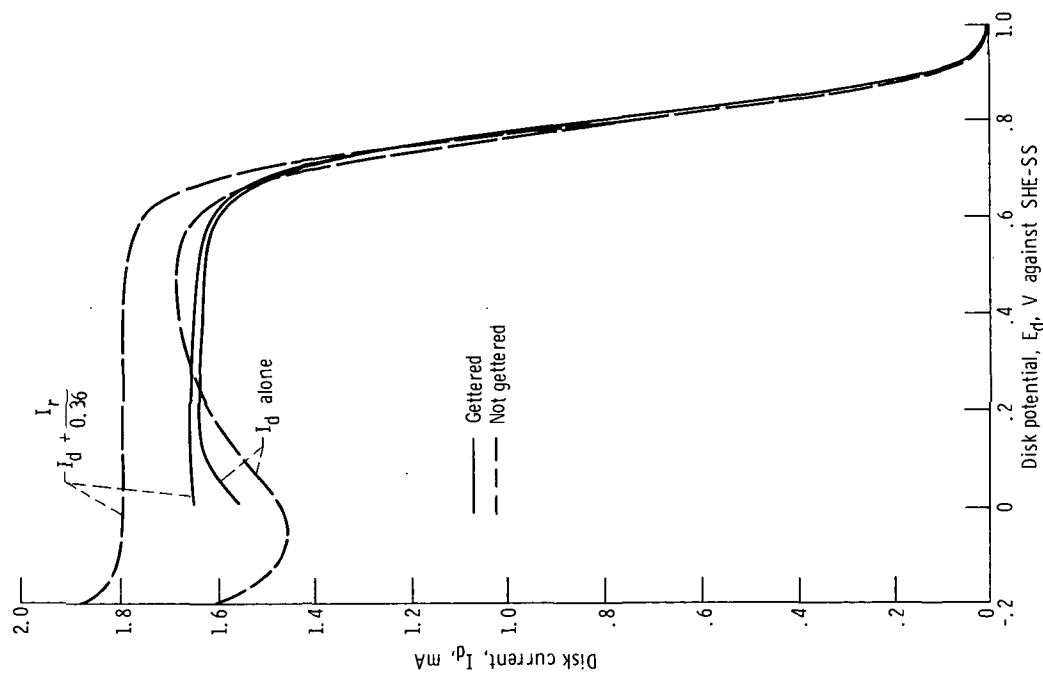


Figure 1. - Effect of gettering 0.1 M potassium hydroxide. Anodic sweeps; 15 volts per hour; rotational speed of electrode, 60 revolutions per second.

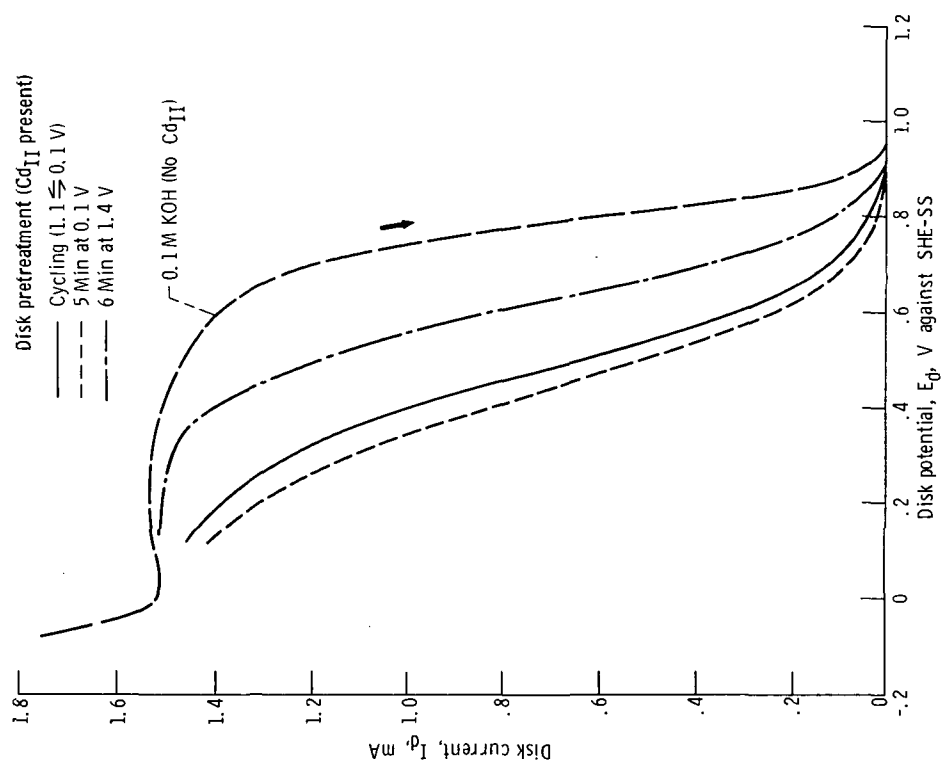


Figure 2. - Effect of cadmium chloride (10^{-4} M $CdCl_2$ added) and disk pretreatment in 0.1 M potassium hydroxide. Anodic sweeps, 50 volts per hour; rotational speed of electrode, 60 revolutions per second.

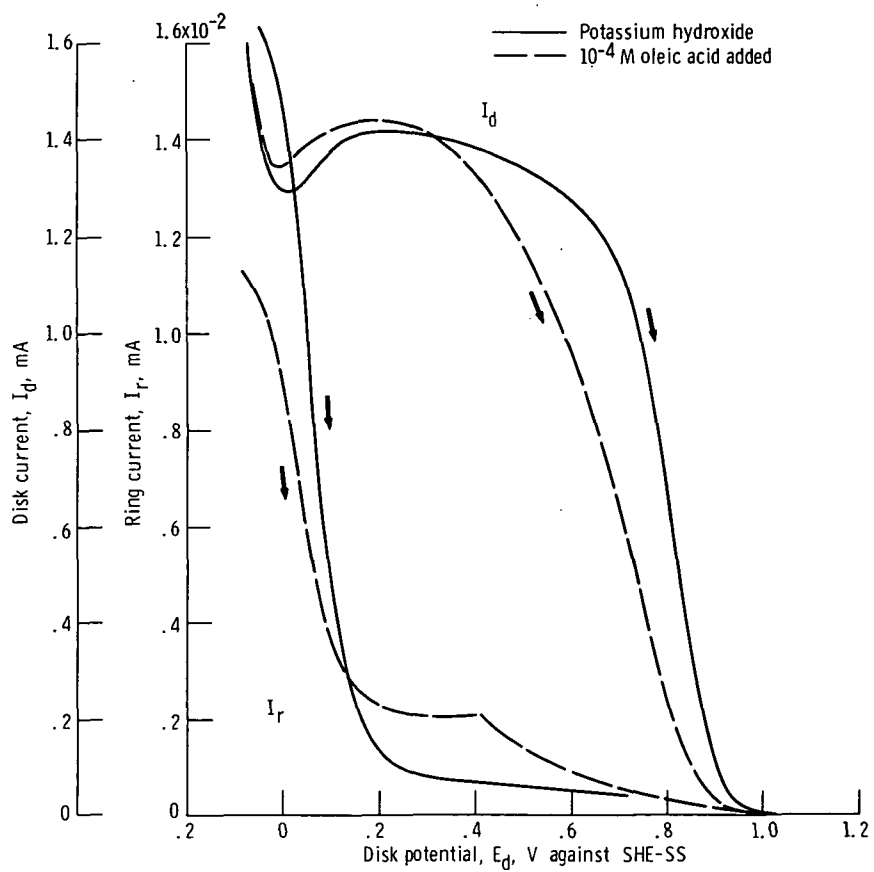


Figure 3. - Effect of oleic acid on ungettered 0.1 M potassium hydroxide. Anodic sweeps, 50 volts per hour; rotational speed of electrode 60 revolutions per second.

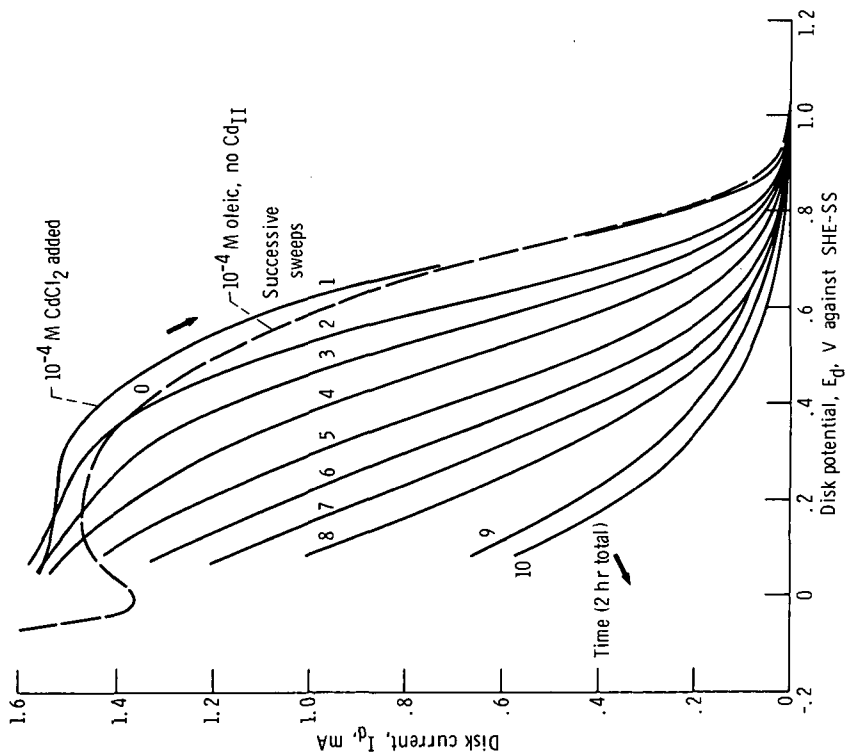


Figure 4. - Progressive poisoning of disk caused by addition of cadmium chloride (CdCl_2) to 0.1 M potassium hydroxide already containing oleic acid. Anodic sweeps, 50 volts per hour; rotational speed of electrode, 60 revolutions per second.

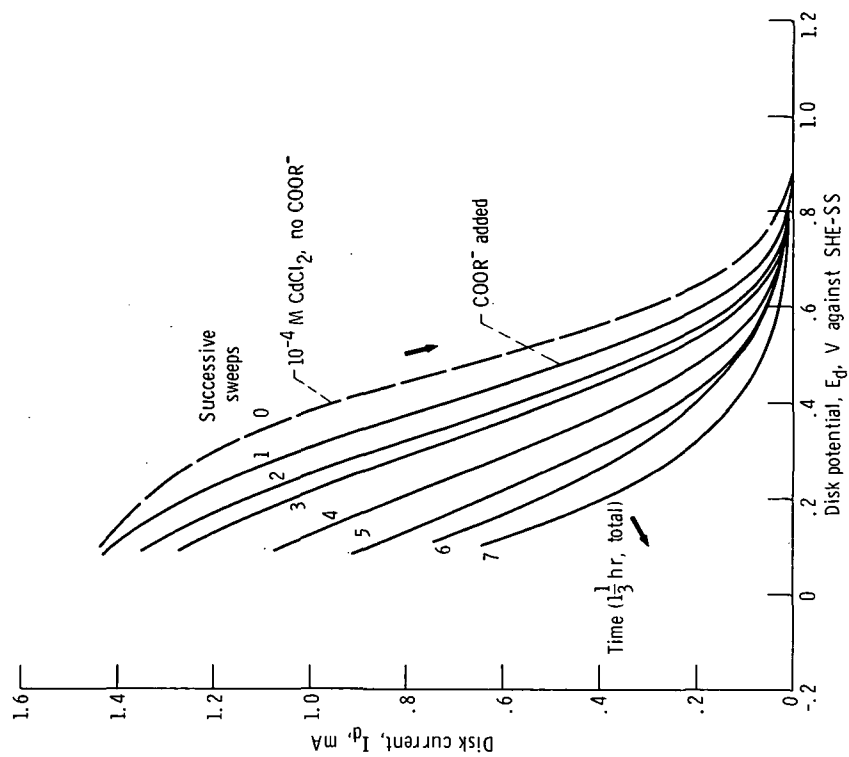


Figure 5. - Poisoning by COOR^- in presence of 10^{-4} M cadmium chloride (CdCl_2); 0.1 M potassium hydroxide. Anodic sweeps, 50 volts per hour; rotational speed of electrode, 60 revolutions per second.

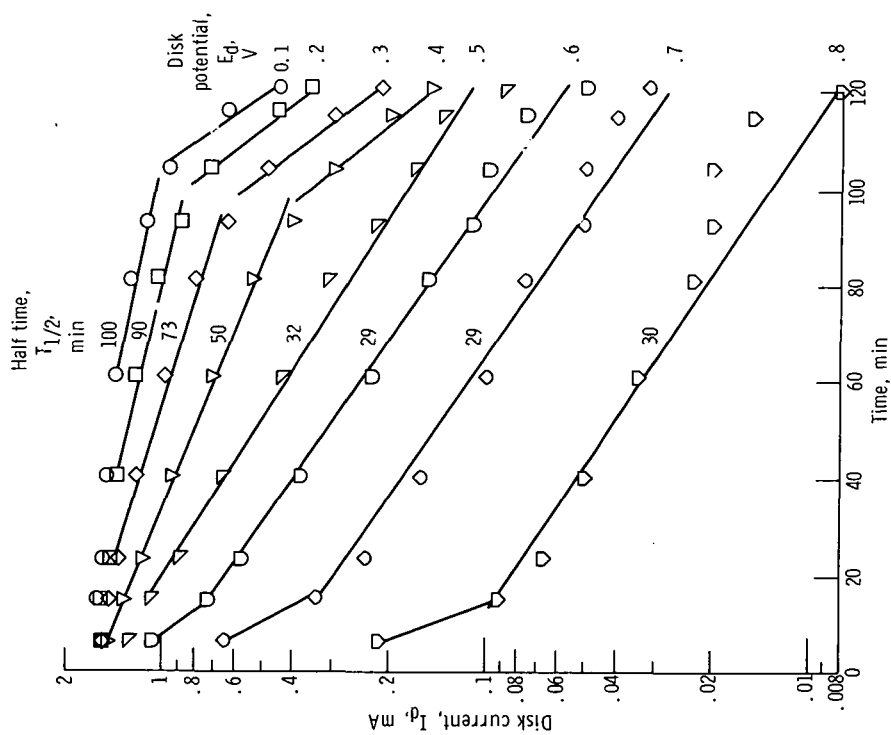


Figure 6. - Decay of disk current after addition of cadmium chloride to 0.1 M potassium hydroxide already containing oleic acid (cross-plot of fig. 4).

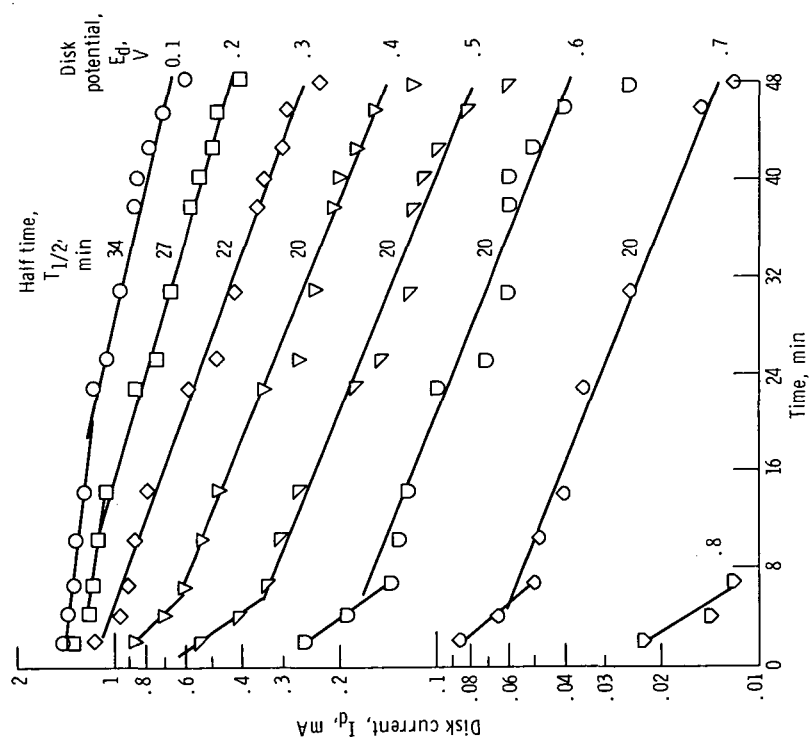


Figure 7. - Decay of disk current after addition of COOR^- to 0.1 M potassium hydroxide plus 10^{-4} M cadmium chloride (crossplot of fig. 5).

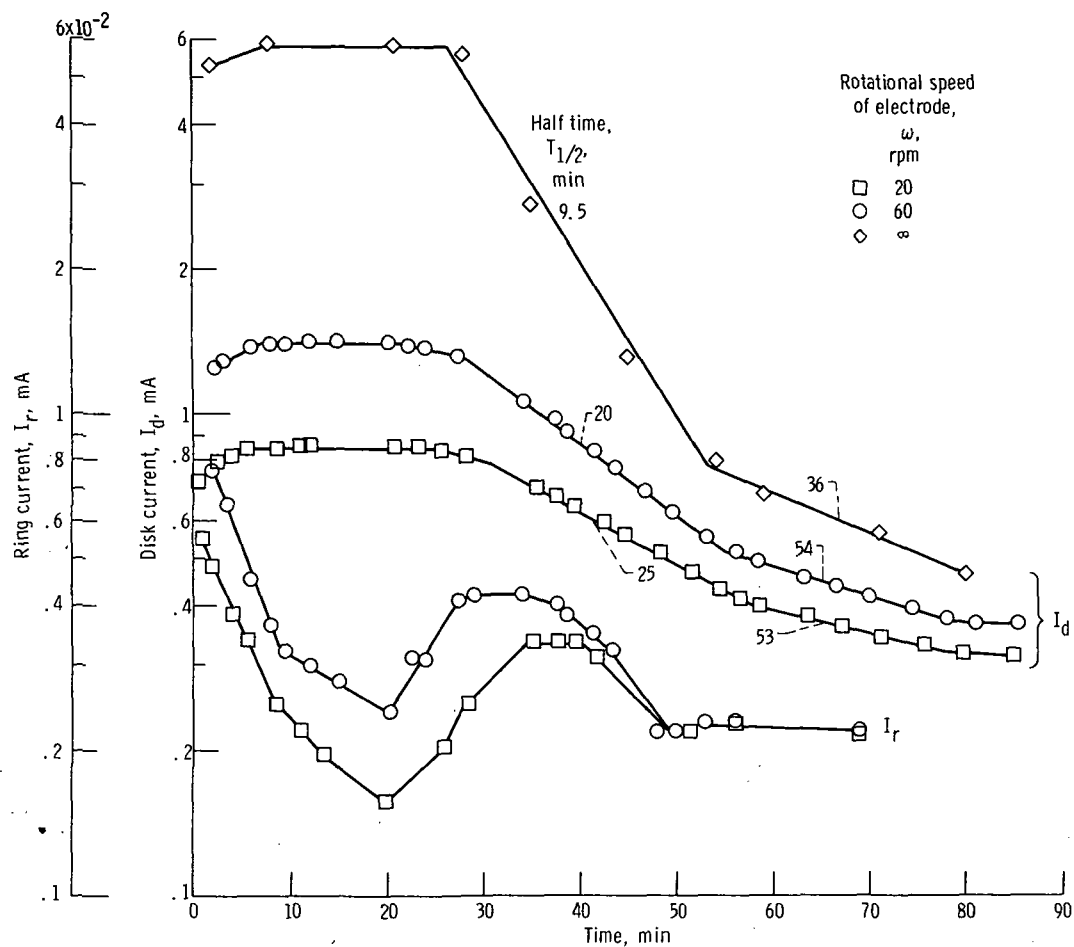


Figure 8. - Effect of time at constant disk potential for 0.1 potassium hydroxide plus 10^{-4} M cadmium chloride and 10^{-4} M oleic acid. Disk potential, 0.100 against SHE-SS.



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—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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